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(19) (CA) **CANADIAN PATENT** (12)

(54) Well Drilling Fluid and Method

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NO DRAWING

Background of the Invention

1. Field of the Invention

5 The present invention relates to drilling fluids and, more particularly, to drilling fluids exhibiting good fluid loss control and stabilization of shale formations.

2. Description of the Background

10 It is known that shale is predominantly formed of clays which swell and disperse when contacted with a water-based drilling fluid. This swelling and dispersion can result in a phenomena known as "heaving" in which the borehole walls can collapse. To reduce this tendency of the clays in the shale to swell and disperse, it is common practice to add cationic salts to render the clays generally hydrophobic. However, in doing this, anionic polymers which are commonly
15 used as viscosifiers in drilling fluids are also rendered hydrophobic, thereby losing their ability to viscosify the drilling fluid or mud and reduce fluid loss from the formation.

20 It is known to use mixtures of cationic polymers and high molecular weight hydroxyethyl cellulose (HEC) when drilling shale formations in order to stabilize the shale by flocculating the clay and impart viscosification. However, prior art cationic drilling mud systems containing HEC suffer from the disadvantages of higher than desired fluid
25 loss and the inability to effectively suspend weighting agents, such as barite, at a viscosity which permits pumping of the fluid.

30 It would therefore be desirable to have a cationic polymer-based drilling fluid which would stabilize the shale, exhibit low fluid loss, viscosify and effectively suspend weighting agents, such as barite.



Summary of the Invention

It is therefore an object of the present invention to provide an improved drilling fluid.

5 Another object of the present invention is to provide a cationic polymer-based drilling fluid exhibiting low fluid loss.

10 Still another object of the present invention is to provide cationic polymer-based drilling fluids which will effectively suspend weighting agents, exhibit low fluid loss and stabilize shale formations.

Yet another object of the present invention is to provide a method of drilling a borehole using a drilling fluid containing a cationic polymer and a low molecular weight hydroxyethyl cellulose polymer.

15 The above and other objects of the present invention will become apparent from the description given herein and the appended claims.

20 The drilling fluid of the present invention comprises an aqueous medium, a water-soluble cationic polymer which will stabilize shale formations, hydroxyethyl cellulose having a molecular weight of from about 3,000 to about 40,000, and a weighting agent. Preferably, the cationic polymer is selected from the group consisting of (a) branched emulsion polymers of diallyldimethylammonium chloride having a molecular weight of at least 5,000, (b) dialkylaminoalkyl acrylic ester polymers, (c) dialkylaminoalkyl methacrylic ester polymers, (d) dialkylaminoalkyl acrylic acid-acrylamide copolymers, (e) dialkylaminoalkyl methacrylic acid-acrylamide copolymers, (f) N-(Dialkylaminoalkyl) acrylamide polymers, (g) N-(Dialkylaminoalkyl) methacrylamide polymers, (h) poly(2-vinylimidazoline), (i) poly(alkyleneamines), (j) poly(hydroxalkylene polyamines) and mixtures thereof.

35 In cases where the aqueous medium contains a salt of a multivalent cation, the drilling fluid will also contain a non-water-swelling clay which is added to the drilling fluid prior to commencement of drilling or picked up by the drilling fluid, in situ, during the drilling operation.

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In the method of the present invention, the drilling fluid described above is circulated in the borehole during the drilling operation.

Description of the Preferred Embodiments

The aqueous medium used in the drilling fluid compositions of the present invention can be fresh water, brines of monovalent cations, such as sodium chloride solutions, potassium chloride solutions, brines of multivalent cations, such as calcium chloride solutions, sea water, etc. The nature of the aqueous medium, as seen hereafter, determines the composition of the drilling fluid.

The cationic polymers which are useful in the compositions and method of the present invention are those cationic polymers which will stabilize, i.e. prevent erosion or dispersion, shale containing water-swellable clays so as to prevent heaving during the drilling operation, which are substantially water-soluble, or dispersible in the aqueous medium, and which act to effectively suspend weighting agents, such as barite. The cationic polymers will be present in amounts ranging from about 0.5 to about 3 pounds per barrel (ppb) of the aqueous medium. Non-limiting examples of suitable cationic polymers include (a) branched emulsion polymers of diallyldimethylammonium chloride having a molecular weight of at least 5,000, (b) dialkylaminoalkyl acrylic ester polymers, (c) dialkylaminoalkyl methacrylic ester polymers, (d) dialkylaminoalkyl acrylic acid-acrylamide copolymers, (e) dialkylaminoalkyl methacrylic acid-acrylamide copolymers, (f) N-(Dialkylaminoalkyl) acrylamide polymers, (g) N-(Dialkylaminoalkyl) methacrylamide polymers, (h) poly(2-vinylimidazoline), (i) poly(alkyleneamines), (j) poly(hydroxalkylene polyamines) and mixtures thereof.

The diallyldimethylammonium chloride polymers useful in the compositions and method of the present invention can be homopolymers or copolymers of other monomers such as acrylamides. Preferably, the polymers are branched emulsion-type polymers which can employ branching agents such as triallylamine, tetraallylammonium chloride as well as bis-diallylammonium salts such as tetraallylpyridinium chloride and N,N,N',N'-tetraallyl-N,N'-dimethylhexamethylenediammonium chloride. The emulsion

polymers can be prepared by emulsion or suspension polymerization techniques such as those described in U.S. Patent No. 3,968,037, and may contain from about 95 to about 99.99 mole percent diallyldimethylammonium chloride and from about 0.01 to about 5 mole percent of one of the aforementioned branching agents. The branched emulsion polymers can have molecular weights ranging from 5,000 and upward, such branched emulsion polymers wherein the molecular weight is from about 40,000 to about 5,000,000 being preferred. Especially preferred are homopolymers of dimethyldiallylammonium chloride having a molecular weight of from about 1,000,000 to about 5,000,000.

Another cationic polymer especially suitable for use in the compositions and method of the present invention are the N-(Dialkylaminoalkyl) acrylamide polymers, such as, for example, polymers prepared via the Mannich Reaction wherein a polyacryl-amide is reacted with formaldehyde and an amine to produce an aminomethylated polyacrylamide. Especially preferred are such polyacrylamides having molecular weights ranging from about 40,000 to about 4,000,000.

Another preferred type of cationic polymer for use in the compositions and method of the present invention are the dialkylaminoalkyl derivatives of a water-soluble copolymer formed from an ethylenically unsaturated amide monomer and a comonomer selected from the group consisting of acrylic acid, alkyl-substituted acrylic acids and mixtures thereof, such as, for example, the copolymer of acrylamide and methacrylic acid. Such polymers, which can have molecular weights ranging from 40,000 to 4,000,000, can be produced, for example, by the method described in U.S. Patent No. 3,923,756. A particularly preferred class of copolymers are the dialkylaminoalkyl acrylamide-methacrylic acid copolymers wherein the copolymer has a molecular weight ranging from about 40,000 to about 4,000,000. Especially preferred, non-limiting examples of such polymers include the dimethylaminoethyl sulfate and chlorides of copolymers of

acrylamide and methacrylic acid.

5 It has been found that the molecular weight of the particular cationic polymer has very little effect on the polymer's ability to stabilize the shale or suspend the weighting agent. Thus, as noted above, cationic polymers of widely varying molecular weights can be employed.

10 The compositions of the present invention also employ hydroxyethyl cellulose as a viscosifier and fluid loss control additive. The HEC, which will generally be present in the compositions in amounts ranging from about 0.5 to about 3 pounds per barrel, preferably 0.5 to 2.5 pounds per barrel, of the aqueous medium, must have a molecular weight ranging from about 3,000 to about 40,000 depending upon the degree of viscosification desired. HEC's having higher
15 molecular weights cannot be used to form weighted muds as per the compositions of the present invention.

In cases where the drilling fluid of the present invention contains a salt of a multivalent cation, e.g., calcium chloride, sea water or the like, it is necessary, in
20 order to achieve acceptable fluid loss control, to include a non-water-swellaable clay. Such clays can be dispensed with if the aqueous medium is fresh water or contains only the salt of a monovalent cation, such as sodium chloride. The non-water-swellaable clay can be added to the drilling fluid at the commencement of the drilling if the formation through
25 which the drilling progresses does not contain a non-water-swellaable clay. Alternately, the clay can be picked up, in situ, by the drilling fluid during the actual drilling operation since many formations contain such non-water-swellaable clays which form part of the drill cuttings. The
30 non-swellaable clay will normally be present in the drilling fluid in amounts ranging from about 1 to about 15 pounds per barrel of the aqueous medium. Suitable, non-limiting examples of such non-water-swellaable clays include kaolin, attapulgit, s p i l i t, et .
35

Th compositions f th present inv nti n also include a wat r-insolubl w ighting agent such as barit, although ther weighting agents such as galena, h matite and oth r

mineral materials may be employed. The weighting agent will generally be present in the compositions in amounts of from about 1 to about 300 pounds per barrel of the aqueous medium.

5 The compositions of the present invention may contain other materials or additives, such as additional viscosifiers or fluid loss control additives, salts, etc. to tailor the mud to desired needs.

10 In the method of the present invention, the drilling fluid, if the formation contains a non-water-swella-
ble clay, is circulated in the well bore, the non-swella-
ble clay being incorporated in situ into the drilling fluid.
Alternatively, the drilling fluid having added non-swella-
ble clay is circulated in the borehole during the drilling
15 operation, this being the method utilized when the formation through which the borehole is being drilled is devoid of non-water-swella-
ble clay.

To more fully illustrate the invention, the following non-limiting examples are presented.

20 Example 1

A series of drilling muds were prepared of varying compositions and tested. In all cases, unless otherwise indicated in this and all the other examples, the muds were prepared by mixing 20 minutes on a Multimixer® following by
25 hot rolling for 16 hours at 150°F prior to testing. The compositions of the drilling fluids and test results are shown in Table 1 below.

A

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Table 1

Formulation	Mud No. 1	Mud No. 2	Mud No. 3	Mud No. 4	Mud No. 5a	Mud No. 5b	Mud No. 5	Mud No. 6	Mud No. 7	Mud No. 8	Mud No. 9	Mud No. 10
Tap water, bbl	.75	.75	.75	.75	.75	.75	.75	.75	.70	.70	.70	.65
KCl, lb	21	21	21	21	21	21	21	21	21	21	21	21
LV 214 283 E ¹ , lb	1	1	1	1	1	1	1	1	1	1	1	1
HEC-QP ² 300, lb	1.5	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
HEC-QP ³ 400, lb	-	1.5	-	3.0	-	-	-	-	-	-	-	-
ZEONEL ⁴ , lb	10	10	10	10	10	10	10	10	10	10	10	10
XC Polymer ⁵ , lb	.25	.25	.25	.25	.25	.25	.25	.25	.25	.25	.25	.25
BAROID ⁶ , lb	200	200	200	200	200	200	200	200	300	300	300	400
Kaolin, lb	-	-	-	-	-	-	-	-	-	-	-	-
BARABRINE DEFOAM ⁷ , lb	.2	.2	.2	.2	.2	.2	.2	.2	.2	.2	.2	.2
Plastic Viscosity, c	15	18	23	20	47	16	37	42	17	20	56	83
Yield Point, lb/100 sq ft	11	14	12	Thick	13	4	6	10	5	10	19	37
10-sec gel, lb/100 sq ft	11	4	6	To	3	5	2	2	4	4	3	4
10-min gel, lb/100 sq ft	45	19	40	Mix	7	7	3	3	7	7	4	7
Fluid Temperature, °F	74	74	74	On	74	74	74	74	74	74	74	74
pH	8.4	8.4	8.4	Multi	8.0	7.8	8.4	8.4	7.4	7.4	7.4	7.5
API Fluid Loss, ml	16	12.5	6.0	Mixer	8.2	50+	4.6	5.0	11	7.2	5.2	4.8
Mud wt, lb/gal	13.0	13.0	13.0	13.0	-	-	13.0	13.0	14.5	14.5	14.5	16.0

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¹Aqueous solution of 7.7 molar (cationic activity) of dimethylaminoethyl sulfate salt of acrylamide-methacrylic acid copolymers having a molecular weight of 4,000,000.

²Trademark for HEC marketed by Union Carbide having a molecular weight of 3,000.

³HEC marketed by Union Carbide having a molecular weight of 40,000.

⁴Trade mark for Non-water-swelling clay marketed by NL Baroid, Inc.

⁵Trademark for Barite weighting agent marketed by NL Baroid, Inc.

⁶Trademark for Mud defoamer marketed by NL Baroid, Inc.

⁷Trademark for Heteropolysaccharide marketed by Kelco Rotary

As can be seen from the data in Table 1, the drilling fluids of the present invention exhibit excellent rheological properties and fluid loss control. With reference to Mud No. 4, it can be seen that when too much HEC having a higher molecular weight, e.g., 40,000, is present, the drilling fluid becomes unacceptably thick. Indeed, it has been found that using HEC's having molecular weights of several million makes it virtually impossible to formulate an acceptable drilling fluid containing a water-insoluble weighting agent. Although Mud No. 4a shows acceptable rheological properties, it has been found that it shows very poor shale stability indicating the necessity of the presence of the cationic polymer to achieve shale stability. Note that when the HEC is not present (Mud No. 4b), there is virtually no fluid loss control. The data in Table 1 also demonstrates that the weighted muds can contain up to 400 pounds per barrel of the weighting agent and still be an acceptable drilling fluid. However, it is to be noted (See Mud No. 10) that the yield point of such heavily weighted mud is higher than would normally be desired.

Example 2

Several drilling fluid formulations were prepared and tested. The compositions of the muds and the test results are shown in Table 2 below.

Table 2

	<u>Formulation</u>	<u>Mud No. 1</u>	<u>Mud No. 2</u>
5	Tap water, bbl	0.7	0.7
	Sea Salt, lb	11	11
	LV 214 283 E, lb	1	1
	HEC-10, lb	-	-
	HEC-QP 300, lb	3.0	3.0
10	BAROID, lb	300	300
	XC Polymer, lb	-	-
	ZEOGEL, lb	-	15
	BARABRINE DEFOAM, lb	.2	.2
	Premix (1 bbl Tap Water		
15	100 lb Kaolin), bbl	-	-
	Plastic Viscosity, cP	60	54
	Yield Point,		
	lb/100 sq ft	22	21
	10-sec gel,		
20	lb/100 sq ft	3	4
	10-min gel,		
	lb/100 sq ft	4	7
	Fluid Temperature, °F	74	74
	pH	7.5	7.4
25	API Fluid Loss, ml	50±	6.0
	Mud wt, lb/gal	14.5	14.5

This example shows that when salts of multivalent cations, such as are contained in sea salt are present, a non-water-swellable clay must be present in order for the drilling fluid to exhibit acceptable fluid loss properties. As can be seen, when no ZEOGEL is present (Mud No. 1), there is virtually no fluid loss control. The results in Table 2 are to be contrasted with the results in Table 1 wherein the aqueous medium contain only the salt of a monovalent cation (KCl) and wherein acceptable fluid loss control could be achieved even in the absence of any non-water-swellable clay (see Mud No. 9 in Table 1).

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Example 3

5 A series of drilling fluids were prepared by mixing the ingredients for 20 minutes on a multimixer. The drilling fluids were then hot rolled for 16 hours at 150°F and tested. The compositions of the muds and the test results are shown in Table 3 below.

Table 3

Formulation	Mud		Mud		Mud		Mud		Mud		Mud		Mud		Mud		Mud		Mud	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10
5 Tap water, bbl	.70	.70	.70	.70	.70	.70	.70	.70	.70	.70										
KCl, lb	21	-	-	21	-	-	21	21	-	-										
NaCl, lb	-	30	-	-	30	-	-	-	-	-										
Seasalt, lb	-	-	11	-	-	11	-	-	-	11										
E-905 ¹	1	1	1	1	1	1	1	1	1	1										
E-904 ² , lb	-	-	-	-	-	-	-	-	-	-										
HEC-QP 300, lb	3	3	3	3	3	3	-	-	-	-										
ZEOGEL, lb	15	15	15	15	15	15	15	15	15	15										
BAROID, lb	300	300	300	300	300	300	300	300	300	300										
XC Polymer, lb	.25	.25	.25	.25	.25	.25	.25	.25	.25	.25										
Mud Temperature, °F	75	75	75	75	75	75	75	75	75	75										
Plastic Visc sity, cp	42	50	53	45	49	50	15	11	14	9										
Yield Point, lb/100 sq ft	29	17	43	20	22	40	35	54	36	41										
10-sec gel, lb/100 sq ft	13	5	29	14	7	27	20	24	24	22										
20 10-min gel, lb/100 sq ft	57	30	71	46	37	67	22	27	22	20										
pH	8.2	8.1	7.7	8.2	8.0	7.7	7.6	7.5	7.6	7.5										
API Fluid Loss, ml	7.5	6.8	10.5	10.5	10.0	13.5	50+	50+	50+	50+										
Mud wt lb/gal	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.5										

25 ¹Trademark of an aqueous solution of 20 molar percent (cationic activity) of a homopolym r of dimethyldiallylammonium chloride having a molecular weight of 40,000 and marketed by Calgon Corp.

²Trademark of an aqueous solution of 15 molar percent (cationic activity) of a homopolymer of dimethyldiallylammonium chloride having a molecular weight of 2,000,000 and marketed by Calgon Corp.

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As can be seen from the data in Table 3, drilling fluids made in accordance with the present invention have excellent rheological properties and exhibit good fluid loss control. Note that when there is no low molecular weight HEC (Mud Nos. 7-10), there is essentially no fluid loss control.

Example 4

To demonstrate that the drilling fluids of the present invention are effective in stabilizing shale, a series of drilling fluids were prepared and compared with a conventional prior anionic polymer-based drilling mud commonly used where shale stabilization is important. In testing the ability of the drilling fluids to stabilize the shale, Pierre shale samples weighing 15 grams and having a diameter between 0.08 and 0.19 inches were hot rolled at 150°F over a six day period. The shale sample was removed from each drilling fluid and re-weighed periodically to determine the amount of erosion that was occurring. The mud compositions and test data are shown in Table 4 below.

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Table 4

	<u>Formulation</u>	<u>No. 1</u>	<u>No. 2</u>	<u>No. 3</u>	<u>No. 4</u>	<u>No. 5</u>
5	Tap water, bbl	1	1	1	1	1
	KCl, lb	25	25	25	25	25
	KOH, lb	0.5	0.5	0.5	0.5	0.5
	HEC-QP 300, lb	3.0	-	-	-	3.
	E-905, lb	1	-	-	-	-
10	Drispac ¹ , lb	-	-	1.5	-	-
	PAC-L ² , lb	-	-	1.0	1.5	-
	EZ-MUD ³ , lb	-	1	-	1	1
	THERM-CHEK ⁴ , lb	-	3	-	-	-
	Kaolin, lb	10	10	5	10	10
15	% erosion values at various times					
	6 hr	0	0	0	1	0
20	24 hr	9.0	9.2	15.5	28.5	15.2
	48 hr	27.4	29.2	53.5	53.6	38.9
	72 hr	47.0	47.8	73.5	70.1	55.2
	144 hr	77.4	-	89.3	88.6	78.5

25 ¹Trade mark of carboxymethyl cellulose marketed by NL Baroid, Inc.

²Trademark of a low molecular weight carboxymethyl cellulose marketed by NL Baroid, Inc.

30 ³Trade mark of a partially hydrolyzed polyacrylamide (anionic polymer) marketed by NL Baroid, Inc.

⁴Trademark of a sulfonated acrylamide copolymer marketed as a fluid loss additive by NL Baroid, Inc.

35 Mud No. 2 is a commonly used prior art anionic polymer-based drilling fluid used in drilling shal formations. While as can be seen, Mud No. 2 shows acceptable shale stabilization, it cannot be effectively weighted with weighting agents such as barite or other generally non-

5 water-soluble weighting agents. On the other hand, Mud No. 1 made in accordance with the present invention is equally as effective at shale stabilization and as shown in previous data can be easily weighted with barite. As can also be seen, drilling fluids which contain neither the cationic polymer nor HEC are not effective at stabilizing the shale (see Mud No. 3 and Mud No. 4). It can also be seen (Mud No. 5) that unless both the cationic polymer and the low molecular weight HEC are present, the drilling fluids are not as effective in stabilizing the shale, even in the presence of an anionic polymer commonly used for shale stabilization.

10 It can thus be seen that the drilling fluids of the present invention are effective at shale stabilization, exhibit low fluid loss and can be easily weighted with commonly used, generally water-insoluble weighting agents such as barite.

15 The foregoing disclosure and description of the invention is illustrative and explanatory thereof, and various changes in the method steps may be made within the scope of the appended claims without departing from the spirit of the invention.

What Is Claimed Is:

5 1. A drilling fluid comprising an aqueous medium, from about 0.5 to about 3 pounds per barrel of said aqueous medium of a water-soluble cationic polymer, from about 0.5 to about 3 pounds per barrel of said aqueous medium of hydroxyethyl cellulose having a molecular weight of from about 3,000 to about 40,000, and from about 1 to about 300 pounds per barrel of said aqueous medium of a generally water-insoluble weighting agent.

5 2. The drilling fluid of Claim 1 wherein said cationic polymer is selected from the group consisting of (a) branched emulsion polymers of diallyldimethylammonium chloride having a molecular weight of at least 5,000, (b) dialkylaminoalkyl acrylic ester polymers, (c) dialkylaminoalkyl methacrylic ester polymers, (d) dialkylaminoalkyl acrylic acid-acrylamide copolymers, (e) dialkylaminoalkyl methacrylic acid-acrylamide copolymers, (f) N-(Dialkylaminoalkyl) acrylamide polymers, (g) N-(Dialkylaminoalkyl) methacrylamide polymers, (h) poly(2-vinylimidazoline), (i) poly(alkyleneamines), (j) poly(hydroxalkylene polyamines) and mixtures thereof.

10

3. The drilling fluid of Claim 2 wherein said branched emulsion polymer has a molecular weight of from about 40,000 to about 5,000,000.

5 4. The drilling fluid of Claim 3 wherein a member selected from the group consisting of triallylmethylammonium chloride, tetraallylammonium chloride, tetraallylpiperazinium chloride and N,N,N',N',-tetraallyl-N,N'-dimethylhexamethylen diammonium chlorid is utilized as a branching agent in forming said branched emulsion polymers, said branched polymers containing from about 95 to about 99.99 mole percent diallylmethylammonium chloride and from about 0.01 to about 5 mole percent of said branching agent.

10

5. The drilling fluid of Claim 1 wherein said water-soluble cationic copolymer comprises a dimethylaminoalkyl acrylamide-methacrylic acid copolymer.

6. The drilling fluid of Claim 5 wherein the molecular weight of said dimethylaminoalkyl acrylamide-methacrylic acid copolymer is from about 40,000 to about 4,000,000.

7. The drilling fluid of Claim 1 wherein said weighting agent comprises barite.

8. The drilling fluid of Claim 1 wherein said aqueous medium contains a salt of a monovalent cation.

9. The drilling fluid of Claim 1 wherein said aqueous medium contains a salt of a multivalent cation and said drilling fluid contains a non-water-swellaable clay.

10. A method of drilling an earth borehole comprising circulating in said borehole during the drilling operation a drilling fluid comprising an aqueous medium, from about 0.5 to about 3 pounds per barrel of said aqueous medium of a water-soluble cationic polymer, from about 0.5 to about 3 pounds per barrel of said aqueous medium of hydroxyethyl cellulose having a molecular weight of from about 3,000 to about 40,000, from about 1 to about 300 pounds per barrel of said aqueous medium of a generally water-insoluble weighting agent and from about 1 to about 15 pounds per barrel of said aqueous medium of a non-water-swellaable clay.

11. The method of Claim 10 wherein said cationic polymer is selected from the group consisting of (a) branched emulsion polymers of diallyldimethylammonium chloride having a molecular weight of at least 5,000, (b) dialkylaminoalkyl acrylic ester polymers, (c) dialkylaminoalkyl methacrylic ester polymers, (d) dialkylaminoalkyl acrylic acid-acrylamide copolymers, (e) dialkylaminoalkyl methacrylic acid-acrylamide copolymers, (f) N-(Dialkylaminoalkyl) acrylamide polymers, (g) N-(Dialkylaminoalkyl) methacrylamide polymers, (h) poly(2-vinylimidazoline), (i) poly(alkyleneamines), (j) poly(hydroxalkylene polyamines) and mixtures thereof.

12. The method of Claim 11 wherein said branched emulsion polymer has a molecular weight of from about 40,000 to about 5,000,000.

13. The method of Claim 12 wherein a member selected from the group consisting of triallylmethylammonium chloride, tetraallylammonium chloride, tetraallylpiperazinium chloride and N,N,N',N',-tetraallyl-N,N'-dimethylhexamethylenedimonium chloride is utilized as a branching agent in forming said branched emulsion polymers, said branched polymers containing from about 95 to about 99.99 mole per cent diallylmethylammonium chloride and from about 0.01 to about 5 mol per cent of said branching agent.

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14. The method of Claim 13 wherein said water-soluble cationic polymer comprises dimethylaminoalkyl acrylamide-methacrylic acid copolymer.

15. The method of Claim 14 wherein the molecular weight of said dimethylaminoalkyl acrylamide-methacrylic acid copolymer is from about 40,000 to about 4,000,000.

16. The method of Claim 10 wherein said weighting agent comprises barite.

17. The method of Claim 10 wherein said aqueous medium contains a salt of a monovalent cation.

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